

## Turn on ESPT: Novel salicylaldehyde based sensor for biological important fluoride sensing



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### ABSTRACT

A novel and simple salicylaldehyde based anion fluorescent sensor **1** has been designed, which can selectively sense fluoride by ‘turn on’ excited-state intermolecular proton transfer (ESPT). The binding constant and the stoichiometry were obtained by non-linear least-square analysis of the titration curves.

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## 1. Introduction

Recently, much attention has been paid on the anion recognition [1–4], and considerable efforts have been devoted to design and synthesis of functionalized receptors for the development of potential anion chemosensors [1–4]. Of particular interest concerning anion sensing is the fluoride ion, due to its well-established role in treatment of osteoporosis and dental care [5,6]. To date, although several sensing systems for fluoride have been reported [7,8], most of them are fluorescent ‘turn off’ sensor. Generally, fluorescence enhancement is favorable to the sensitivity in the sensing process, compared to those displaying fluorescence quenching, because the false results, derived from other quenchers, maybe reported by fluorescent ‘turn off’ sensor in practical samples [9].

Furthermore, numerous signal mechanisms [4], such as intramolecular charge transfer (ICT), photoinduced electron transfer (PET), excimer/exiplex, metal-to-ligand charge transfer, competitive binding and fluorescence resonance energy transfer (FRET), have been developed to design anion fluorescent sensors. However, excited-state intra/intermolecular proton transfer (ESPT), as a well-documented signal mechanism [10–12], has scarcely been used in anion recognition and sensing [13–17]. In fact, ESPT occurs in the excited state through an intramolecular hydrogen bonded ring [10–12], in which proton/hydrogen is transferred to an electronegative atom. And ESPT molecules are employed extensively

in photostabilizers, lasers, optical devices and information processing.

Hydrogen bonds were used extensively in the design of charge neutral anion receptors, especially for NH group [1,2], such as amide, urea, thiourea, sul-fonamide, pyrrole and indole. However, only few anion sensors involved the OH groups to obtain the anion binding and sensing [1,2]. In addition, the OH acidity of receptor maybe dramatically improved upon photoexcitation [13–17], and thus the ESPT channel could be open by anion binding [10,13].

On the basis of the above-mentioned background, herein we designed and synthesized a new compound **1** containing OH group. Sensor **1** exhibited the high selectivity for the biologically important F<sup>−</sup>, and ‘turn on’ ESPT was suggested to be the signal mechanism.

## 2. Experimental

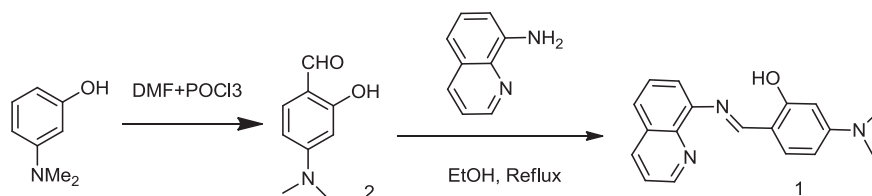
### 2.1. Materials and equipments

Commercially available 3-(dimethylamino)phenol and quinalin-8-amine were purchased from Aladdin, China. Other reagents for synthesis were used without further purification. All anions in the form of tetrabutylammonium salts were obtained from Sinopharm Chemical Reagent Co. Ltd., stored in a desiccator under vacuum. Acetonitrile for spectroscopy was obtained from the J&K Scientific Ltd.

Absorption spectra were recorded on a Shimadzu UV2550 spectrophotometer. Fluorescence spectra were carried out on Shimadzu

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**Scheme 1.** Synthesis of sensor **1**.

RF-5301PC spectrofluorometer.  $^1\text{H}$  NMR was determined in  $\text{DMSO-}d_6$  on a Bruker 400 MHz spectrometer using TMS as internal standard. High resolution mass spectrum was performed on an Agilent 1200 time-of-flight mass spectrometer. C, H, N elemental analyses were made on Elementar Vario-III elemental analyzer.

## 2.2. Synthesis of receptor **1**

4-(Dimethylamino)salicylaldehyde was prepared by the reported procedure [18] with little modification. To a dry DMF solution (21.0 ml) containing 3-(dimethylamino)phenol (3.10 g, 22.6 mmol) was added  $\text{POCl}_3$  (4.0 ml, 43.2 mmol) at  $0^\circ\text{C}$ . The mixture was stirred for 10 min, and further stirred for 30 min at room temperature. Then the resulting mixture was stirred overnight at  $80^\circ\text{C}$ . After cooling, the reaction mixture poured into ice-cold water. The solution was neutralized using saturated  $\text{Na}_2\text{CO}_3$ , and the formed precipitate was filtered off, washed several times with water and dried under vacuum. m.p.  $80.1\text{--}81.2^\circ\text{C}$  [19];  $^1\text{H}$  NMR

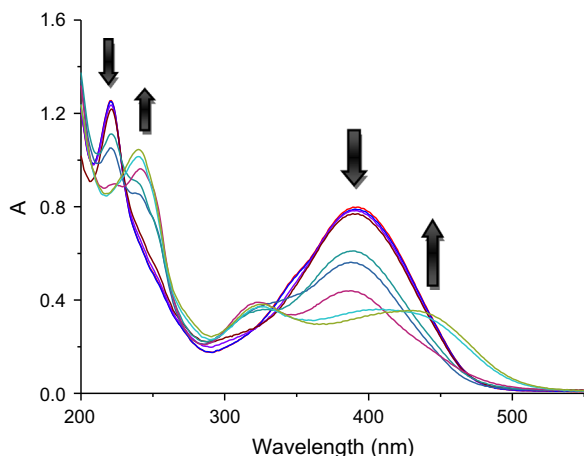
(400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.09 (s, 6H, CH<sub>3</sub>), 6.10–7.29 (m, 3H, Ar–H), 9.53 (s, 1H, OH), 11.61 (s, 1H, CHO).

Quinolin-8-amine (0.36 g, 2.5 mmol) and compound **2** (0.41 g, 2.5 mmol) were mixed in dry methanol (25 ml). The mixture was refluxed for 3 h under  $\text{N}_2$ . Then the methanol was evaporated and the residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1:3) to give sensor **1** in 65.2% yield as green–brown solid.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  3.02 (s, 6H, CH<sub>3</sub>), 5.96–6.37 (m, 3H, Ar–H), 7.30–8.82 (m, 6H), 9.12 (s, 1H, CH=N), 13.97 (s, 1H, OH); ESI-MS: 292.1417 ( $\text{M} + \text{H}^+$ ); Anal. calcd. for  $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}$ : C, 74.18; H, 5.89; N, 14.39; O, 5.54 (see Scheme 1).

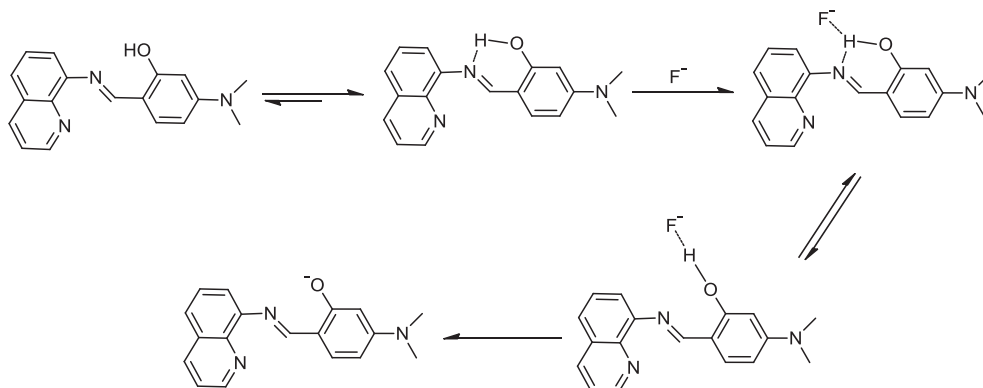
## 3. Results and discussion

### 3.1. UV–VIS spectral response of sensor **1**

To establish the anion binding and sensing affinities of sensor **1**, spectrophotometric titration experiments have been performed by adding a standard solution of various anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HSO}_4^-$ ,  $\text{NO}_3^-$  and  $\text{AcO}^-$ , tetrabutylammonium salts, TBA) to  $\text{CH}_3\text{CN}$  solution of sensor **1** at room temperature. As shown in Fig. 1, sensor **1** itself displayed two maximum absorption bands at  $\sim 220$  nm and  $\sim 391$  nm, which can be assigned to  $n\text{--}\pi^*$  and  $\pi\text{--}\pi^*$  transition [19] favored by the planar orientation enforced by intramolecular hydrogen bonding (Scheme 2) [7,13,20], respectively. Upon addition of  $<1.0$  equiv.  $\text{F}^-$  to the solution of sensor **1**, the peak at  $\sim 220$  nm and  $\sim 391$  nm decreased insignificant. And with further increasing amount of  $\text{F}^-$ , two peaks fell gradually and vanished, at the same time, the new peaks at  $\sim 240$  nm,  $\sim 328$  nm and  $\sim 431$  nm occurred. Considering the strong basicity of  $\text{F}^-$  [21] and high stability of  $[\text{HF}_2]^-$  complex [7,13], these spectral changes were presumably ascribed to the first hydrogen bond interaction between sensor **1** and  $\text{F}^-$  [1], and subsequently, the deprotonation of OH at the sensor **1** [7,13,21]. This suggested the formation of negatively charged  $\text{PhO}^-$  of sensor **1**, which resulted in the substantial increase on charge density of sensor **1** [1], and the enhancement in push–pull effect of intramolecular charge-transfer in the ground state [1]. To substantiate the assumption,



**Fig. 1.** Changes in UV–VIS absorption spectra for sensor **1** ( $4.0 \times 10^{-5}$  mol/l) upon addition of TBAF (0–60.0 equiv.).



**Scheme 2.** Proposed binding mode of sensor **1** with  $\text{F}^-$ .

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